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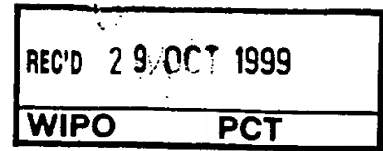
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# Kongeriget Danmark

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Fremgangsmåde til metallisering af overfladen på et fast polymersubstrat samt produktet opnået herved

A method of metallizing the surface of a solid polymer substrate and the product obtained

5 The present invention relates to a method of metallizing the surface of polymer substrates such as polyolefins, polyalkylenes, polyarylenes and mixtures thereof and the product obtained.

10 Polymer surfaces with low surface energy such as untreated or unmodified polymer substrates are in general difficult to metallize.

15 It is well-known in the art to clean the surface of a polymer substrate or to modify the surface of the substrate in order to change the surface characteristics of the substrate and thereby improve the affinity between the substrate surface and a metal.

20 The surface treatment methods normally used depends on the initial surface energy of the substrate to be treated. Wet methods comprise etching with chromic acid or sulfochromic acid, chemical treatment with a solution of stannous chloride, or a solution containing metals  
25 such as Ag, Pd, and Au. All of these treatments are very rough methods which may weaken the cohesiveness of the polymer substrate. Further, it is normally preferred to avoid the use of strong acids in industrial environments.

30 Among dry methods, the generally used method is corona treatment. By use of this method a number of small sparks are created between the substrate surface and a counter electrode (a silent discharge). These sparks often result in an erosion of the surface as well as in a generation  
35 of free radicals. The formed free radicals are normally terminated by reaction with ambient oxygen. One of the

problems regarding this method is, that it is not suited for treatment prior to metallizing strongly curved surfaces or surfaces with many cavities.

5 A method of electroless plating is described in JP application No. 92-240189. In this method a PTFE substrate is irradiated with UV laser in the presence of amine or amide followed by an immersing in an electroless metal plating solvent. This results in a good bonding of the  
10 plated metal to the substrate. However, this method is very difficult to control and also very expensive.

US 3 956 535 discloses a method of metallization where the object to be metallized is coated with a film having  
15 incorporated therein a hydrolyzed metal complex. Upon this metal complex a metal or metal ion is adsorbed and acts as catalyst for autocatalytic metal deposition. This method is not usable on many types of polymer substrates due to poor adhesion between the coated film and the sub-  
20 strate.

US 4 952 286 describes another expensive method which includes immersing an article to be plated into an electrolytic bath containing dissolved plating metal. Before im-  
25 mersing, the surface has been provided with areas of catalytic metal chalcogenide coating to be converted to a chemical resistant metal-coating.

US 4 057 663 describes a method to make hydrophobic polymers suitable for electroless plating using a concentrate  
30 containing  $P_2O_5$ . This method is particularly suitable for polymers containing fluor, but not very useful for other polymers.

35 US 4 919 768 discloses another expensive method of metallization, where non-conducting surfaces are provided with

a metal sulfide coating, acting as a base for direct electroplating.

Those methods are, however, as indicated very expensive,  
5 complicated to use and not applicable to various types of polymer substrates.

The object of the present invention is to provide an industrially applicable method of binding a metal layer to  
10 a polymer substrate, which method does not comprise the above mentioned problems.

Another object of the present invention is to provide an industrially applicable method of binding a metal layer  
15 to a polymer substrate, which method results in a good binding strength, and can be used on most polymer substrates.

Another object of the present invention is to provide a  
20 fast method of binding a metal layer to a polymer surface, and thereby provide a good binding strength.

A further object of the present invention is to provide a method of metallizing a polymer surface, which does not  
25 result in any severe depolymerization of the polymer substrate, in particular when the substrate material exhibits fluorine and/or tertiary carbon atoms, and by use of which method the surface affinity against the metal is improved.

30 A further object of the present invention is to provide a metallized polymer surface, which can be enhanced by electrochemical deposition using any conventional method.

35 A further object of the present invention is to provide a method for metallizing a polymer substrate, which method

is environmentally acceptable, and results in a good binding strength.

Another object of the present invention is to provide a method for metallizing a polymer substrate, which method is economical acceptable.

A further object of the present invention is to provide a method for metallizing a polymer substrate, which method is uncomplicated to use.

These objects are achieved by a method of metallizing a surface of a solid polymer substrate comprising the steps of

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a) generating radicals on the substrate surface by subjecting it to a gas plasma,

b) treating the surface with a vapour of one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrolates, such as acrylic acid, triethylen glycol diacrylat, glycidyl acrylat, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylat, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allylalcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea(thiosine-amine).

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c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and

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d) optionally providing a metallization of the surface by using a conventional electroless bath, or

avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization,

where step b) starts before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follows immediately after step a), where step c) starts before step b), simultaneously with step b), follows immediately after step b) or within 8 months after step b), preferably within 6 months, and where step d) follows step c) or starts simultaneously.

The method is preferably carried out in a reactor which may be at least partly evacuated from air and water vapour. Further, the reactor should have a channel for feeding the working gas, and a channel for feeding the monomer or monomer mixture. The monomer or monomer mixture is introduced as a gas, e.g. by evaporation from a bottle or by injection, e.g. through a nozzle.

In a preferred embodiment of the invention, the substrate is placed in the reactor, and some or all of the air and optionally water vapour are evacuated.

Gas is fed into the reactor, and the plasma is generated (step a). Before, simultaneously or shortly thereafter monomer or monomer mixture is fed into the reactor (step b)).

The generation step a) is preferably carried out for a period of between 0,01 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and

60 seconds, and the treatment step b) is preferably carried out for a period of between 0,1 and 1000 seconds, preferably between 1 and 500 seconds, more preferably between 10 and 200 seconds.

5

The treatment step b) may continue when step a) has ended, even though there no longer are generated radicals on the substrate surface. This continuation of step b) will then result in a polymerisation of monomers onto the monomers which already have been bound to the polymer surface.

If the surface of the polymer substrate is contaminated with water, oil or other organic contaminants, step a) is preferably carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a) so as to clean the surface before the monomers are polymerised onto the substrate surface. Step a) and b) are preferably ended simultaneously.

20

The partial pressure of the gas or the plasma in step a) is preferably between 0.1 and 10000 Pa.

The monomer pressure in step b) is preferably between 0.1 and 100000 Pa, more preferably between 10 and 1000 Pa.

25

The total pressure, i.e. the sum of the partial pressures of the air, optionally water vapour, the gas or plasma and the monomer, under step a) is preferably equal to the total pressure under step b), the total pressure is preferably between 0.2 and 100000 Pa, more preferably between 0.2 and 10000 Pa, and most preferably between 10 and 1000 Pa.

30

The temperature is not important but should preferably be the same under both step a) and step b). Normally the

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temperature will rise slightly during the generation step a). Preferably the temperature under both step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.

5

The polymer substrate can be of any polymer material provided that free radicals are created on the surface of the material when it is subjected to a gas plasma or other means of radical generation. Preferably the polymer  
10 substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene type, such as polybutadiene, polyisoprene, a silicone type, such as silicone rubber, a fluorine type, such as polytetrafluorethylene or its copolymers.

15

The substrate can have any shape and any size, and may comprise complicated geometries. Preferably the polymer substrate is in the form of film, sheet, pipe, rod, porous or non-porous body, fabric, non-woven fabric, fibres  
20 or threads and/or as profiles made by extrusion, compression moulding, injection moulding, thermoforming or vacuum forming.

The generation of radicals on the substrate surface is  
25 preferably obtained by subjecting the substrate to a gas plasma. The plasma can be generated by any known methods, but preferably the gas plasma is generated by excitation of a gas in a direct current (DC), low frequency (LF), radio frequency (RF) or microwave (MW) generated electric  
30 field. Most preferably the gas plasma is generated by excitation of a gas in a direct current (DC) or by excitation using low frequency (LF).

The intensity of the used gas plasma should preferably  
35 have a level ensuring creation of radicals in the polymer surface. If the level is too high, this may result in se-

vere damage of the bulk-polymer (depolymerization). Hence, the power level of the plasma should be optimised so that surface radicals are created, but no serious damage is made to the bulk.

5

A preferred method of generating a plasma is described in the applicant's European patent application No. EP 96610018.2.

10

#### *Experimental systems*

Although it is possible to carry out all necessary steps in a single vacuum vessel, initial experiments were carried out in two separate systems. In one of the systems the virgin polymer surface was altered by the use of a plasma treatment using a working gas and monomers. In the other vacuum system metal atoms were subsequently deposited to the surface of the test samples. Although possible in an industrial production, the approach of using separate machines for the two steps is highly inefficient. The results obtained from these experiments do, however, reflect the results obtainable if a custom made system, able to perform both tasks is used.

25

The first step was on all samples carried out in an experimental plasma system, essentially consisting of a 22 litre vacuum vessel having two inlet channels for gas and for monomer, respectively, and an electrode arrangement as described above with reference to the applicant's EP application No. 96610018.2 The plasma is generated using the 3-phase technique described above with a frequency of 50 Hz and  $U_0$  of 240 to 280V. 27 electrodes are arranged in a circle around the vacuum vessel with a diameter of 17 cm. Every third of the electrodes is connected to  $U_r$ , another every third of the electrodes is connected to  $U_s$ ,

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and the last every third of the electrodes is connected to  $U_t$ .

The second step was on all samples carried out in an experimental plasma system, essentially consisting of a glass bowl having an internal volume of 15 litres. To atomise the metal and transfer it from the target to the sample surface a custom made magnetron was constructed. The magnetron is essentially a copper plate, having a diameter of 10 cm and a thickness of 4 mm. The back-side of the copper plate is shielded using a ceramic container. On the backside of the copper-plate a magnet is mounted. The magnetron is operated by applying a negative DC potential of 450 V. During operation a current of 0.05 A is drawn between the magnetron and the positive parts of the chamber. During all experiments argon is used as the working gas for the magnetron.

Both plasma systems are pumped using the same vacuum system comprising an Edwards EH 250 Roots-blower, backed by an Alcatel rotary vane pump. The pressure is monitored using an Alcatel pirani-gauge, mounted on the start of the pumping-line.

During step a) and b) the sample is held at floating potential.

#### Example 1

Covering a 100x50x3 mm sheet of polytetrafluorethylene (PTFE) with a conductive layer of metal.

#### Step 1

The sheet was subjected to an argon plasma, generated as described above, for 20 s at a pressure of 0.1 mbar.

Hereafter a vapour essentially comprising of 2-ethyl cyano acrylate and glycidylmetacrylate was let into the argon plasma at a pressure of 0.15 mbar for 30 s.

5    Step 2

After this treatment 100  $\mu\text{m}$  of silver (Ag) was deposited onto the surface, making the surface conductive. The deposition was accomplished by using a silver sheet as a target on the magnetron, and the magnetron was operated  
10    for 60 seconds.

Step 3

After Ag deposition, the sheet was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless  
15    copper"). Due to the combined treatment in step 1 and 2 an adherent copper coating was formed where Ag was deposited.

The copper layer can be 0.5  $\mu\text{m}$  or more, depending on the  
20    treatment time in the electroless copper bath. The average thickness obtained after a given time is as claimed by Shipley 2.5  $\mu\text{m}$  per hours.

The adhesion strength of the copper layer was examined by  
25    the standard well known to people skilled in the art, DIN 53 151 having a scale from GT 0 to GT 5, where zero is excellent. The treated sample in this example complied the standard and got the score Gt 0 - Gt 1.

30    Example 2

Covering of a component made from polypropylene (PP) with a shielding metallic layer.

35    Step 1

The component was subjected to an argon plasma as described above for 10 s at a pressure of 1 mbar. Hereafter a vapour essentially comprising of toluene-2,4-diisocyanate was let into the plasma chamber at a pressure of 2 mbar for 20 s.

#### Step 2

After this treatment 2 ML (monolayers) of platinum (Pt) was accomplished by using a Pt sheet as a target on the magnetron, and the magnetron was operated for 5 seconds.

#### Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Pt was deposited on the PP component.

#### Example 3

Covering a PTFE surface with a 0.5  $\mu\text{m}$  metal layer.

Steps 1 and 2 were conducted as described in example 2.

#### Step 3

The component was immersed in an electroless copper bath, ("Shipley Cuposit 251 electroless copper"). Due to the combined treatment in steps 1 and 2 an adherent copper coating was formed where Ag was deposited.

#### Example 4a

Covering a PTFE surface with a 5  $\mu\text{m}$  metal layer.

Steps 1 - 2 identical to the steps in example 2.

Step 3

Copper was then deposited on the Ag covered surface using a conventional electroplating technique.

5

Example 4b

Covering a PTFE surface with a 5  $\mu\text{m}$  metal layer

10 Steps 1 - 3 identical to the steps in example 3

Step 4

More copper was then deposited on the surface using a conventional electroplating technique.

15



## CLAIMS.

1. A method of metallizing a solid polymer substrate comprising the steps of

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a) generating radicals on the substrate surface by subjecting it to a gas plasma,

b) treating the surface with a vapour of one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrylates, such as acrylic acid, triethylen glycol diacrylate, glycidyl acrylate, isocyanates, such as 1,4-diisocyanobutane, toluenediisocyanate, epoxy compounds, such as glycidyl methacrylate, preferably 2,3-epoxypropyl methacrylate, allylic and vinylic compounds, such as vinyl acetic acid, vinyl norbonene, vinyl pyrrolidone, vinyl trimethoxysilane, vinyl trimethylsilane allylene, allyl alcohol, allyloxymethylsilane, allylphenol, allylurea 1-allyltheourea(thiosineamine),

20

c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and

25

d) optionally providing a metallization of the surface by using a conventional electroless bath, or

avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization;

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where step b) starts before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follows immediately after step a), where step c) starts before step b), si-

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multaneously with step b), follows immediately after step b) or within 8 months after step b), preferably within 6 months, and where step d) follows step c) or starts simultaneously with step d).

5

2. A method according to claim 1, wherein the catalytic metal comprises Pt, Ag, Pd, Cu and Au.

3. A method according to claim 1, wherein the monomer or  
10 monomer mixture comprises one or more of cyanoacrylate and glycidyl metacrylate, preferably 2,3-epoxypropyl methacrylate.

4. A method according to each of the preceding claims 1,  
15 2 or 3, wherein step b) comprises treatment of the surface with a monomer vapour comprising 0.5 to 90 mole-%, preferably between 10 and 60 mole % of 2-ethyl cyanoacrylate vapour.

20 5. A method according to claim 4, wherein the monomer prior to the vaporisation consists essentially of 2-ethyl cyanoacrylate, an acid having a partial vapour pressure in the plasma which is lower than the partial vapour pressure of 2-ethyl cyanoacrylate, and up to 40 weight-%  
25 of another filler, preferably an acid having a partial vapour pressure in the plasma which is lower than half the partial vapour pressure of 2-ethyl cyanoacrylate, most preferably the acid is a polyphosphoric acid and is present prior to the vaporisation in a concentration up  
30 to 10 weight-%.

6. A method according to each of the preceding claims, wherein the polymer substrate is a polyolefine type, such as PE, PP, or an aryl type, such as styrene, a diene  
35 type, such as polybutadiene, polyisoprene, a silicone

type, such as silicone rubber, a fluorine type, such as polytetrafluorethylene or its copolymers.

7. A method according to each of the preceding claims 1-  
5 5, wherein the polymer substrate is a PTFE and PP.

8. A method according to each of the preceding claims,  
wherein the polymer substrate is an injection moulded  
polymer component, a polymer fibre, a polymer thread or a  
10 polymer filler.

9. A method according to each of the preceding claims,  
wherein step a) comprises the generation of radicals by  
use of a gas plasma generated by excitation of the gas in  
15 a direct current (DC), low frequency (LF), audio frequency (AF), radio frequency (RF) or microwave generated electric field.

10. A method according to each of the preceding claims,  
20 wherein the monomer pressure in step b) is between 0.1 and 100000 Pa, preferably between 10 and 1000 Pa.

11. A method according to each of the preceding claims,  
wherein the generation step a) is carried out for a period  
25 of between 0.01 and 1000 seconds, and the treatment step b) is carried out for a period of between 0.1 and 1000 seconds.

12. A method according to claim 11, wherein step a) is  
30 carried out for more than 30 seconds, and step b) is started 10 to 30 seconds after step a).

13. A method according claim 11, wherein the generation  
step a) is carried out for a period of between 10 and 60  
35 seconds, and the treatment step b) is carried out for a period of between 10 and 200 seconds.

14. A method according to each of the preceding claims, wherein the temperature is the same under both step a) and step b), and preferably the temperature under both  
5 step a) and step b) is between 250 and 450 K, most preferably between 280 and 330 K.

15. A method according to each of the preceding claims, wherein the total pressure under step a) is equal to the  
10 total pressure under step b), the total pressure is preferably between 0.2 and 100000 Pa, more preferably between 0.2 and 10000 Pa, and most preferably between 10 and 1000 Pa.

15 16. A polymer substrate metallized according to the method of each of the preceding claims 1-15.

A method of metallizing the surface of a solid polymer substrate and the product obtained

#### ABSTRACT

5

A method of metallization a solid polymer substrate comprising the steps of

10 a) generating radicals on the substrate surface by subjecting it to a gas plasma,

b) treating the surface with a vapour of one or more monomers comprising monomers selected among cyano acrylate, mono- and diacrylates, isocyanates, epoxy compounds,  
15 pounds, allylic and vinylic compounds,

c) providing a short surface deposition using a PVD or CVD process to deposit metal atoms, such as copper, tin, silver palladium, platinum, or gold, and  
20

d) optionally providing a metallization of the surface by using a conventional electroless bath, or

25 avoiding electroless metallization by using direct electrolytic metallization, when the metal layer formed in c) has a thickness allowing electrolytic metallization,

where step b) starts before step a) provided that step b) does not terminate until step a) is started, simultaneously with step a), under step a), or follows immediately  
30 after step a), where step c) starts before step b), simultaneously with step b), follows immediately after step b) or within 8 months after step b), preferably within 6 months, and where step d) follows step c) or starts simultaneously with step d).  
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